

(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 694 548 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

31.01.1996 Bulletin 1996/05

(51) Int. Cl.<sup>6</sup>: C07F 5/00, C07F 5/06

(21) Application number: 95110913.1

(22) Date of filing: 12.07.1995

(84) Designated Contracting States:

BE DE ES FR GB IE NL

(30) Priority: 29.07.1994 IT MI941635

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(54) Organometallic derivatives of group IIIA and process for their preparation

(57) New organometallic derivatives of group IIIA are described having general formula  $M(C_6F_5)_3$  wherein M is a metal of group IIIA selected from aluminium, gallium and indium.

The above derivatives are prepared by exchange reaction between a metal alkyl  $MR_3$  with an organometallic derivative of boron having the formula  $B(C_6F_5)_3$ .

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In the preferred embodiment,  $m = 3$ .

The organometallic compound of boron,  $B(C_6F_5)_3$ , used as reagent in scheme (A), was prepared as already described in scientific literature, by reacting a derivative of magnesium having the formula  $(C_6F_5)_2Mg \cdot Br$ , obtained from  $C_6F_5-Br$  and  $Mg$  in flakes, with  $BF_3 \cdot Et_2O$  in ethyl ether.

5 The compound  $M(H)_nR_m$  is a derivative of di- or tri-alkyls of Aluminium, Gallium or Indium.

This can also be obtained with the methods already described in scientific literature, but in the case of aluminium, valid derivatives which can be used for the purposes of the present invention, such as for example:  $Al(CH_3)_3$ ,  $Al(C_2H_5)_3$ ,  $Al(i-C_4H_9)_3$ ,  $AlH(i-C_4H_9)_2$  are already available on the market.

10 The reaction according to scheme (A) is carried out in a basically aliphatic, cycloaliphatic or aromatic, hydrocarbon solvent, by mixing solutions of the reagents  $B(C_6F_5)_3$  and  $M(H)_nR_m$  in the above solvents.

The molar ratios of the reagents indicated in scheme (A) are maintained, for reasons of convenience, simplicity of the reaction and purity of the final product  $M(C_6F_5)_3$ , at basically 1:1.

In fact, if an excess of the reagent  $B(C_6F_5)_3$  is used, part of this must be recovered at the end of the reaction as it is the most expensive component; in addition the isolation of the desired product in its pure state is more difficult.

15 If, on the contrary, an excess of the component  $M(H)_nR_m$  is used, the purity of the final product is jeopardized as, at the end of the reaction, besides the expected products  $B(H)_nR_m$  and  $M(C_6F_5)_3$ , there will also be consistent quantities of mixed products of the type  $M(C_6F_5)_nR_{3-n}$  with  $n=1$  and  $2$ .

The reaction temperature is not determinant for obtaining the final product if the reaction is carried out within the range  $-20/+100^\circ C$ . It is preferable however to operate at a temperature of between  $0$  and  $+30^\circ C$ .

20 In general, the reaction is carried out by dissolving the derivative  $B(C_6F_5)_3$  in toluene or hexane and adding, under stirring, to the solution thus obtained, a solution of  $M(H)_nR_m$  in the same solvent. Basic solvents must be avoided or those which would sensitively interact with the derivatives of Boron or the metal of group IIIA (for example amines, water, alcohols, ethers).

25 As all the compounds involved, reagents and products, are highly sensitive to oxygen or humidity, or both, all the reaction phases and subsequent isolation of the desired product, must be strictly carried out under an inert gas using the well-known nitrogen-vacuum technique.

After a time ranging from a few seconds to several hours, depending on the type of  $R$  and  $M$  and solvents used, the solution becomes turbid because of the formation of an abundant white precipitate consisting of the desired product  $M(C_6F_5)_3$  in its pure state. The quantity of the product  $M(C_6F_5)_3$  which precipitates depends on the operating conditions used and varies from 40% to 70% of the equivalents of the metal used in the reaction. After this first precipitation the mother liquor of the reaction can be concentrated at room temperature or cooled to a low temperature obtaining further quantities of microcrystalline product. The final yield of dried crystallized product varies from 70% to 90%, calculated on  $M(H)_nR_m$  used as reagent.

35 As already specified above, the reaction solvent basically consists of an aliphatic, cycloaliphatic or aromatic hydrocarbon from which the product precipitates and can be recovered by filtration and subsequent drying under vacuum for several hours.

When an aromatic solvent is used, for example toluene or benzene, the final product, recovered as a crystalline solid after drying at room temperature, contains a mole of solvent per mole of derivative and the final product is therefore better represented by the general formula  $M(C_6F_5)_3 \cdot (\text{solvent})$ . The molecule of solvent can be easily removed if the drying step is carried out under vacuum at  $80^\circ C$ , without the desired final product,  $M(C_6F_5)_3$ , undergoing any decomposition, as shown from chemical analyses and NMR and infrared spectra.

When, on the other hand, an aliphatic solvent is used, the drying of the recovered solid can be carried out directly at room temperature under the vacuum of a mechanical pump, to obtain the desired product without the solvent.

40 In the case of  $Al(C_6F_5)_3$ , the chemical nature of the product, was identified not only by chemical analyses of the solid, but also by means of its infrared spectrum (fig. 1 and 2) and NMR spectrum of the  $^{19}F$  (fig. 3). The infrared spectrum also permitted the presence of the toluene molecule to be revealed in the crystal obtained by drying at room temperature and its disappearance after heating the crystalline solid to  $80^\circ C$ .

The NMR spectrum of the  $^{19}F$  (in toluene- $d_8$  at 243 K), shown in figure 3, showed that only three signals of fluorine exist in the molecule at  $\delta = -124.6, -152.1, -162.0$  ppm (taking the signal at  $\delta = -78.5$  ppm of the  $CF_3COOD$  in toluene- $d_8$  as external reference), with a relative intensity of 2:1:2. This trend of the spectrum can be explained by attributing the three signals, in order, to the fluorine atoms in ortho, para and meta position with respect to the carbon bound to the aluminium atom in the  $-C_6F_5$  rings. The presence of only three types of resonances for the fluorine atom shows that the three  $C_6F_5$  rings are equivalents and therefore the  $Al(C_6F_5)_3$  compound is monomeric. In fact, the formation of a dimer would cause a differentiation of the  $-C_6F_5$  rings with an increase of the number of signals relating to fluorine.

55 The products having general formula (I), particularly those wherein  $M$  is  $Al$ , can be advantageously used as cocatalysts in the Ziegler-Natta polymerization of olefins and diolefins.

With respect to the enclosed figures, number 1 is the IR spectrum in nujol of  $Al(C_6F_5)_3$  (toluene), figure 2 is the IR spectrum in nujol of  $Al(C_6F_5)_3$  after drying at  $80^\circ C$  for 8hrs under vacuum ( $10^{-5}$  Pa), figure 3 is the NMR spectrum of

g (0.11 moles) of  $\text{Al}(\text{C}_2\text{H}_5)_3$ . Within an hour an abundant precipitate is formed which is filtered, washed twice with hexane, and dried with the mechanical pump at room temperature.

4.0 grams of  $\text{Al}(\text{C}_6\text{F}_5)_3$  are recovered with a calculated yield of 69% of  $\text{Al}(\text{C}_2\text{H}_5)_3$ .

## 5 Claims

1. Compounds having general formula (I)  $\text{M}(\text{C}_6\text{F}_5)_3$ , wherein M is a metal of the group IIIA of the periodic table of elements, selected from Aluminium, Gallium and Indium.
2. Compound according to claim 1, wherein M is Aluminium.
3. Process for the preparation of compounds having general formula (I)  $\text{M}(\text{C}_6\text{F}_5)_3$ , characterized in that  $\text{B}(\text{C}_6\text{F}_5)_3$  is reacted with a compound having formula



wherein:

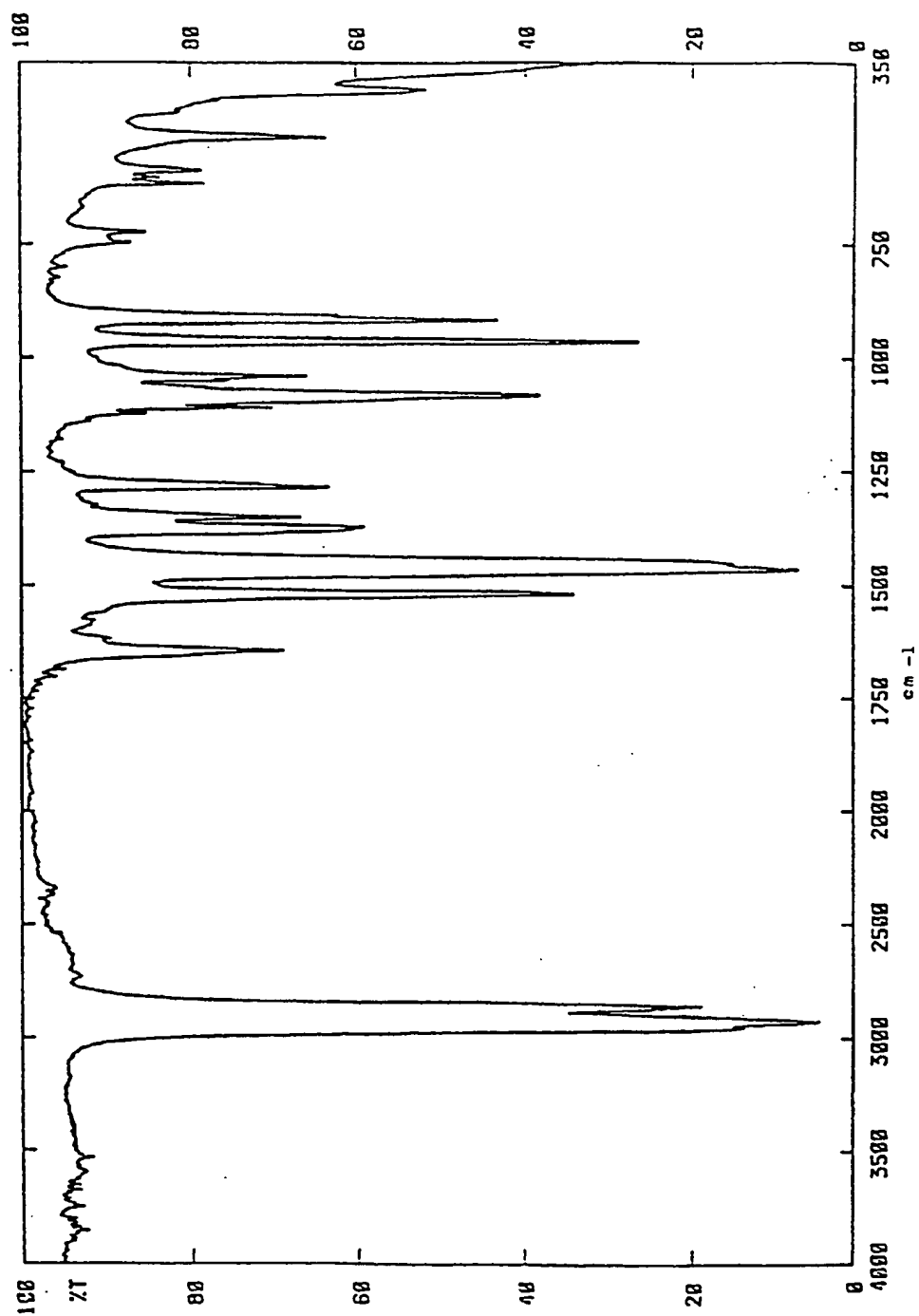
M is a metal of the group IIIA selected from Aluminium, Gallium and Indium;

R is selected from aliphatic, cycloaliphatic, benzylic, linear or branched, monofunctional radicals, containing from 1 to 20 carbon atoms;

$n + m = 3$ ; n is 0 or 1.

4. Process according to claim 3, characterized in that R is selected from methyl, ethyl and isobutyl.
5. Process according to claim 3, characterized in that the molar ratio between  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{M}(\text{H})_n\text{R}_m$  is basically 1 to 1.
6. Process according to claim 3, characterized in that the reaction takes place in a basically hydrocarbon solvent.
7. Process according to claim 3, characterized in that the reaction is carried out at a temperature of between  $-20^\circ\text{C}$  and  $+100^\circ\text{C}$ .
8. Process according to claim 7, characterized in that the reaction temperature is between  $0^\circ\text{C}$  and  $30^\circ\text{C}$ .
9. Process according to claim 3, wherein M is Al,  $m = 3$ , R is selected from methyl, ethyl and isobutyl.

FIG. 2





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# EUROPEAN SEARCH REPORT

Application Number  
EP 95 11 0913

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	J. ORGANOMET. CHEM., vol.441, no.3, 1992 pages 363 - 371 K. LUDOVICI ET AL * page 370, paragraph 2 *	1	C07F5/00 C07F5/06
X	CHEMICAL ABSTRACTS, vol. 75, no. 19, 1971, Columbus, Ohio, US; abstract no. 118363x, * abstract * & AUST. J. CHEM., vol.24, no.9, 1971 pages 1771 - 1779 G.B. DEACON ET AL	1	
X	CHEMICAL ABSTRACTS, vol. 74, no. 23, 1971, Columbus, Ohio, US; abstract no. 125769s, * abstract * & INORG. NUCL. CHEM. LETT., vol.7, no.4, 1971 pages 329 - 331 G.B. DEACON ET AL	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C07F
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 17 October 1995	Examiner Kapteyn, H
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